

DETERMINATION OF BENZENE
IN HYDROCARBONS

BY

W. T. McCAULEY

ARMOUR INSTITUTE OF TECHNOLOGY

1920

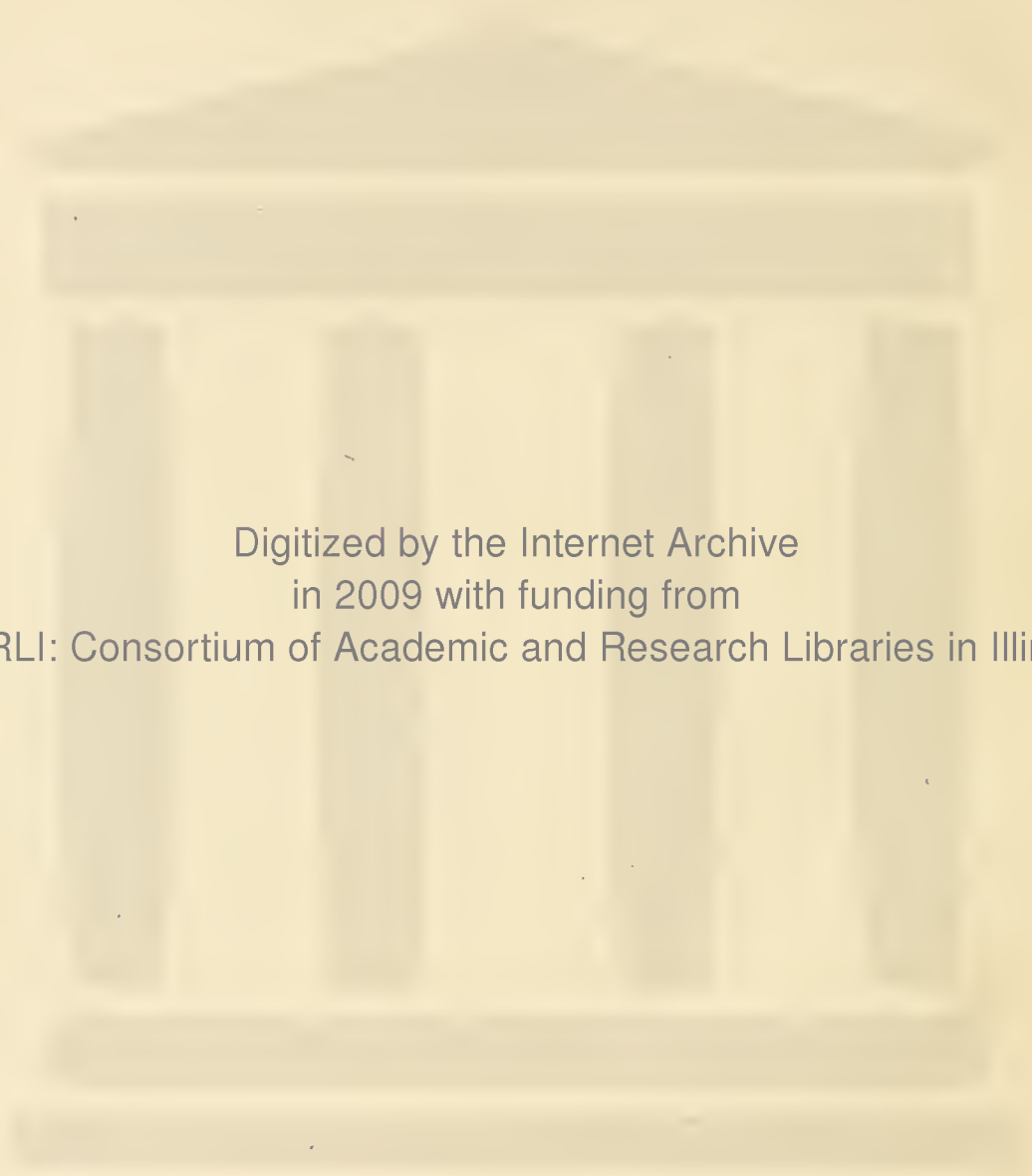
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DETERMINATION OF BENZENE AND ITS DERIVATIVES IN ADMIXTURES WITH PARAFFIN HYDROCARBONS

A THESIS

PRESENTED BY

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TO THE

PRESIDENT AND FACULTY

OF

ARMOUR INSTITUTE OF TECHNOLOGY

FOR THE DEGREE OF

BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

MAY 27, 1920

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Benzene was discovered in 1825 by Faraday, in the liquid obtained from compressed oil gas. In 1846 its isolation from coal tar, one of the important sources, was accomplished by H.W.Hofmann. Since that time , its use has become very extensive.

At one time this hydrocarbon was used principally as a source of supply for other aromatic bodies. This was especially true during the recent war, when the demand for high explosives greatly exceeded the supply. During this critical period all efforts were bent on obtaining benzene and its homologues for use in ammunitions. Every source of supply was utilized regardless of the cost of recovery. But this was an abnormal condition and consequently could not exist after

the emergency had passed. All the processes which were very expensive to operate have been or are being abandoned. The sudden decline in the demand, after a period of intensive production, left a great excess supply which could not be absorbed by the chemical industries, whose demands are normally supplied by recovery from by-product coke-oven installations. An attempt has been made to utilize this excess as a motor, either when in the pure state or when mixed in varying amounts with gasoline.

Since this is the outlook, some method for the determination of benzene when mixed with other components of an oil, especially the paraffin hydrocarbons, must be developed. It must be applicable for general laboratory

use, permitting rapid analysis and accurate results. It is in view of this demand that the present work has been undertaken.

Needless to say there has been previous work done on the quantitative determination of benzene in all sorts of mixtures. A survey of the literature will give a comprehensive view of the mass of material presented, and the difficulty of selecting a method which is suited to the work in hand. The bibliography given in this report includes the important material done on this subject up to the present time.

In the estimation of benzene, its physical and chemical properties form the basis of attack. This being the case most all its properties have at one

time or another been used in an attempt to develop a satisfactory method of analysis. Some of the properties which have been used are: boiling point, freezing point, specific gravity, solubility, refractive index, surface tension, viscosity, "molecular weight" or the effect on the boiling point or freezing point when in solution, and definite chemical reactions such as nitration, sulfonation, etc.

A survey of these methods shows that few of them are practically applicable to the problem at hand. A short and satisfactory summary of them is given by a government publication¹ which is quoted in part:

1). "Manufacture of Gasoline and Benzene-Toluene from Petroleum and Other Hydrocarbons." Bulletin 114. Petroleum Technology 29.

"Surface tension is readily influenced by the presence of small quantities of impurities and, in the absence of definite knowledge concerning its nature, is of little importance. "Molecular weights" have been shown to be unreliable even when determined for mixtures that are chemically more homogeneous than those obtained in the present work.

Separation through differences in boiling point needs little discussion. That benzene, toluene, and xylene can be separated by distillation is indicated by the differences in their boiling points, which are as follows: benzene, $80.4^{\circ}\text{C}.$; toluene, $110.3^{\circ}\text{C}.$; xylene, $138^{\circ}\text{C}.$

However, although the three aromatic hydrocarbons may be separated from each other by retification they cannot be isolated from the aliphatic hydrocarbons that are present in the cracked oil and have boiling points approximately the same as those of benzene, toluene, and xylene. In the determination of the aromatic compounds wide differences between the specific gravities of the aromatic hydrocarbons and those of the other constituents of approximately like volatility were of great aid.

The refractive index is closely related to specific gravity, and on account of that relation did not demand special consideration. Viscosity is not an additive

property. In actual fact, information was needed regarding only the first four of the properties listed.

The use of dimethylsulfate as a solvent has been investigated by Valenta, Perkin and Harrison, Chapin, Reeve and Lewis, Sommer, Church and Weiss, and by Rittman, Twomey, and Egloff. The only logical conclusion to be had from a review of these researches is that this method is not to be recommended.

Owing to the relatively high freezing point of benzene, various investigators have recommended that the benzene content of an oil be quantitatively estimated by a freezing method.

Some experiments, therefore, were conducted with known mixtures of benzene and unrefined gasoline with a specific gravity of 0.728. ----- These results indicate that benzene crystals tend to include so much mother liquor that the freezing method for the determining of benzene is unreliable. It appears also that in the presence of an excess of nonaromatic constituents the benzene crystals may either be prevented from separating out or may be dissolved as soon as formed. In any event the freezing method seems to have little to recommend it.

Prevoius considerations indicate that the most promising physical property on which to base analytical methods was specific gravity. By making use of the differences in gravities of aromatic and non-aromatic hydrocarbons at the same temperatures it was possible to estimate with some accuracy the content of aromatic hydrocarbons. This method required a knowledge of the average specific gravity of nonaromatic constitutents, and values were assumed that had been indicated as the results of much experience. In order to check these the aromatic content of various distillates was determined by the standard chemical method of nitration. A close agreement was noted among results obtained by the two methods --- the tedious one of nitration and the simple one of specific gravity."

According to this information supplied by the Department of Interior, the two methods worth considering are nitration and the determination of the specific gravity.

The method of nitration, which is conceded to be accurate but slow is

described by Lunge¹ as follows:

"Determining available benzene in a mixture. G.Lungy ("Coal Tar and Ammonia", 3rd. English Ed., p.626). recommends the nitration test, which depends on the production of nitrobenzene. He describes it as follows: 100cc of the sample are placed in a 500cc flask provided with a cork carrying two tubes. A mixture of 150 gm. of HNO_3 (sp.g. 1.14), and 180 to 200 gm. of H_2SO_4 (sp. g. 1.84) is prepared and allowed to cool. Portions of this mixture are placed in the stoppered tube and allowed to flow drop by drop into the benzene, shaking this up almost instantly. If the temperature rises, the flask must be cooled by immersion in water. When addition of acid ceases to produce rise in temperature the flask should be heated gently for an hour or two, during which time it will be an advantage to connect the second tube with a reflux condenser. Allow the mixture to settle and separate the layer by a separatory funnel. Most of the crude nitrobenzene is in the upper layer. The lower (acid) layer should be diluted with several times its bulk of water and allowed to stand for a few hours. Any oily liquid separating should be added to the nitrobenzene. Wash the latter with

1)."Allan's Commercial Organic Analysis.

water several times, then with a very dilute solution of NaOH, and once again with water. Care should be taken that none of the product is lost in these washings. The washed nitrobenzene is then allowed to settle, carefully separated, redistilled in a fractionating flask until the temperature of 150° is reached and the distillate once more nitrated, using large excess of the acid mixture. Any material remaining undissolved may be regarded as nonaromatic hydrocarbons. 157.6 parts of nitrobenzene correspond to 100 parts of pure benzene."

In preference to this method the Department of Interior recommends that of specific gravities referring the values obtained to a chart of specific gravity and percentage composition.

In order to approach the accuracy of the nitration method and the speed of the specific gravity determination, W. Mendius¹ recommends that we determine benzene and its derivatives by bromination to dibrombenzene. His method

1). The Determination of Benzene in Petroleum Distillate.

is as follows:

"The specific gravity of the oil to be tested is determined and 0.1cc or about 0.1gm of it is introduced into a clean and dry test bottle, which already contains the 0.02gm of pure 200 mesh iron. The author recommends the use of a bottle as shown in Fig.11. Just enough carbon bisulfide is then added to dissolve the oil, say about 5cc. Enough N/1 bromine solution is added to furnish the bromine for the iron (0.0579gm. Br.) and the bromine to form dibrombenzene (0.360 gm. Br.) assuming the oil to be pure benzene. This is to furnish sufficient excess to brominate. The bottle is immediately stoppered, water sealed and let stand for one hour at 35°C. A blank test should be made with every series of tests to standardize the bromine solution. At the end of one hour the flask is cooled, the stopper removed and washed, and an excess of potassium iodide solution added. The mixture is thoroughly agitated. The free iodine which is liberated by the equivalent amount of bromine not absorbed is titrated with 1/5th normal solution of sodium thiosulfate using starch to aid in the detection of the end point, which is the final disappearance of the blue color. Much agitation is necessary. Knowing the standard and relation of the two solutions the amount of bromine absorbed is calculated. This is the difference between the amount of bromine solution equivalent of the thiosulfate solution, times the standard of the bromine solution. The amount of the bromine

reacting with the iron is subtracted from this amount. The resulting figure is the amount absorbed by the benzene and the olefines. From this is subtracted the amount of bromine absorbed by the olefines ---. The benzene is divided by 4.094 which gives the weight of benzene in the oil. With this data the percentage, by weight, of benzene in the oil can easily be calculated."

This work is based on the above method: the scope of the undertaking being to duplicate the results if possible, and then to apply the method in a general way by using known mixtures.

Benzene of the highest degree of purity was prepared by treating commercial benzol with concentrated H_2SO_4 and dilute caustic: then fractionally distilling; preserving only the benzene fraction. Purification was further continued by distillation until the entire fraction boiled within two degrees of 80°C . Finally the sample was subjected to fractional crystallization until it froze

within 0.1°C of 5.48°C .

The first difficulty encountered in the method was that of getting an accurate sample of benzene either by volume or by weight. Several methods were tried. The first was that of using a burette. This was found to be too inaccurate and permitted the vaporization of the sample. Weighing in Victor-Meyer bottles was tried. This gave an accurate weight, but the size of the mouth of the bottle did not permit sufficient contact to yield good results. Especially prepared bottles, made by blowing very thin walled glass tube into small bulbs, then drawing out the neck to form a very small opening, was tried. These were filled by immersion of the stem of the heated bulb into the benzene, which was sucked up as the bulb cooled. The difficulty in the use of these was due to the burning of the sample when an attempt was made to seal the stem.

Finally satisfactory volumes were obtained by the use of small standardized pipette graduated to 0.01cc. In this way the sample could be introduced into the carbon bisulfide, the solvent contained in the reagent bottle, and the volume of the sample be accurately known.

This search for a satisfactory way of obtaining a sample gave practice in developing the necessary technic. After the use of the pipette as giving the best results was decided upon, several runs were made to develop the proper proficiency in conducting the analysis. Results of this preliminary work are given in table 1. Through out the work the percentage of benzene entering the reaction is expressed on the basis of the formation of monobrombenzene.

The next step was the duplication of the results obtained in the previous work performed

on this subject. That this is possible is shown in the results given in Table III. Table II., obtained in the process of the work done to assemble the data for Table III., indicates that in order to secure consistent results the percent of bromine used for bromination of the benzene must be over 207% of the amount necessary to form monobrombenzene. Tables III. and IV. in addition to proving that the product obtained is dibrombenzene demonstrates that at least 242% bromine is necessary to give uniform results. Also above the concentration of approximately 250% and up to 625% bromine the product is always the dibrom body. Therefore in accordance with this data, the concentration of bromine used will be as near as possible to 250%, but in every case an excess rather than an insufficient amount should be used.

The work done so far proves that on using samples of pure benzene and brominating, we get a uniform product of dibrombenzene, and that from data on the normality of the standard solutions we can quantitatively determine benzene by this method. This brings up the next step, that of trying the method out on known mixtures.

One thousand cc. of commercial gasoline were obtained and purified. The purification process consisted of repeated washing with concentrated H_2SO_4 until the acid remained clear on shaking with the gasoline. A 1% solution of caustic was added to neutralize the excess acid. Water was used for the final washing. The gas was fractionally distilled, saving the portion which boiled between 80° and $140^{\circ}C$. This distillate was dried over calcium chloride.

Since the product cannot be assumed to be free from unsaturated bodies, a test for them must be made. The method used was the standard one as given in Allan¹:

"A 1/10th normal solution of bromine is made by dissolving 2cc of bromine in 750cc of recently distilled carbon disulfide and the solution, having been dried over calcium chloride crystals, is preserved in the dark.

From 0.3 to 1 gram of oil is weighed out in a perfectly dried stoppered flask or separator, the oil diluted if necessary with about 25cc of carbon disulfide. Then 25cc of the bromine solution is added, the flask stoppered, agitated and left in the dark for 15 minutes. If the liquid is not distinctly red after the agitation, a further quantity of bromine solution is added without delay. After 15 minutes an excess of an aqueous solution of KI is poured in, the mixture agitated. The bromine which was not absorbed by the oil having been replaced by an equivalent amount of free iodine, the flask is removed to a light place and the contents titrated with 1/10th normal solution of sodium thiosulfate. The titration is conducted in the usual manner, the final change being rendered more sharp by adding a few drops of starch solution when the

1). Commercial Organic Analysis.

carbon bisulfide is nearly decolorized.

The bromine solution used requires to be standardized occasionally by titrating 25cc. of the bromine solution as above. The difference between the volume of sodium thiosulfate solution now required, and that used after treating the oil, represents the volume corresponding with the amount of bromine absorbed."

The results of this analysis are shown in Table V. The amount of unsaturated hydrocarbons present is expressed as the number of grams of bromine absorbed per cc. of the gasoline. This amount is to be deducted from the total amount of bromine used in the future analyses involving gasoline, just as in the case of the bromine absorbed by the iron in the formation of ferrous bromide.

In order to know how much benzene there was per cc. of the gas, an analysis of it was made following the same prescribed method as given on page 10. The results proved to be satisfactory and are set forth in Table VI.

Mixtures of definite amounts of gas and benzene were made. See Table VII. In the calculations the allowance for the bromine needed to form FeCl_2 and to brominate the unsaturated bodies was made. The total amount of benzene used in the tests is known since it is the sum of the amount of pure benzene plus the amount found to be present in the gasoline.

The results obtained show that the method described permits accurate work, but the accuracy of the results demands careful and accurate work on the part of the analyst.

Several tests were made with a view of making the method more rapid. The use of iron as a carrier necessitates the weighing of a definite amount of iron for each run. This involves time and trouble. In order to overcome this a carrier of another type was tried. A series of runs, with FeCl_3 as a

carrier, were made with the results shown in Table VIII. These figures indicate that the absorption of bromine by benzene is very incomplete and varies within wide ranges, although the conditions are the same.

To add to the safety of the water seal around the stopper, the feasibility of putting a layer of water in the bottle was tried. The accuracy of the results was impaired, and the absorption greatly affected by the presence of the water. See Table IX.

In completing this report a mention of some of the precautions necessary to accuracy will not be out of place.

The data submitted in Table IX. shows that the presence of water is detrimental. Although the discrepancies are not as great when there is only a small amount of water, nevertheless the best results can only be expected when the container and the reagents

are perfectly dry. This detail must be carefully observed. The presence of moisture during the analysis is indicated by the iron adhering to the bottom of the bottle.

The standard solutions used should be of low concentrations. This permits greater accuracy due to the fact that an error of several drops in running out the required amounts is much less than would be the case if a more concentrated solution were used. Especially is this true in the case of the bromine solution for example were it was observed that 10cc of the solution could be drawn from the burette and another several drops drawn out without the level of the meniscus apparently changing. These few drop may cause an appreciable error.

After the time for reaction has been allowed, the bottles should be placed under a cold water tap. This cooling of the bottle

and contents requires about 15 minutes. At the end of this time the bottle may be opened without loss of any of the sample due to the pressure of the vaporized liquids in the bottle.

Titration with an excess of potassium iodide (about 10%) gives a clear end point and more satisfactory results than if less is used. The outline of the method as given on page 10 calls for vigorous shaking. This was not found to be necessary and in fact if the shaking is carried too far the values are greatly impaired. That is to say, with an excess of KI and moderate shaking the best results are obtained. When shaking is carried too far the results obtained were too low indicating that some of the bromine in the dibromobenzene has been replaced by the iodine. This fact is substantiated by the reappearance of the blue color after standing.

In conclusion the method suggested has been found to be satisfactory. The product of bromination is always dibrombenzene. The accuracy of the results is equally good when using pure benzene mixed with other bodies as when using pure benzene. But as mentioned before, care and accuracy on the part of the analyst are a prime essential.

TABLES.

TABLE 1.

Bromination to DiBrombenzene.

Preliminary Tests.

Test No.	Bromine Used		Bromine Absorbed		Benzene		Error
	Wt.	%	Wt.	%	Used	Determined	%
16	5.5564	617.3	2.8062	311.8	.4392	.6847	55.9
17	4.8144	550.7	2.4512	273.5	"	.5980	36.1
18	3.6341	403.7	1.8899	210.0	"	.4611	4.9
19	3.6077	400.8	1.8268	202.7	"	.4457	1.5
20	2.5361	281.8	1.9643	218.1	"	.4792	9.1
21	2.5361	281.8	1.7667	196.1	"	.4310	- 1.9

TABLE 11.

Determination of Percent

Bromine Necessary.

Test No.	Bromine Used		Bromine Absorbed		Benzene		Error
	Wt.	%	Wt.	%	Used	Determined	%
22	1.8613	206.7	1.7029	189.2	.4392	.4155	- 5.40
23	"	"	1.6637	184.8	"	.4059	- 7.59
24	"	"	1.7020	189.1	"	.4152	- 5.40
26	"	"	1.6832	187.0	"	.4106	- 6.52
27	1.7927	199.2	1.6702	185.5	"	.4075	- 7.22

TABLE 111.

Determination of the Best Percent
of Benzene to Use.

Test No.	Bromine Used		Bromine Absorbed		Benzene		Error
	Wt.	%	Wt.	%	Used	Determined	%
29	2.1812	242.4	1.8071	200.6	.4392	.4409	.39
30	"	"	1.8071	200.6	"	.4409	.39
31	"	"	1.8068	200.4	"	.4408	.38
32	"	"	1.8070	200.6	"	.4408	.38
34	2.7707	308.7	1.7939	199.6	"	.4377	- .35
35	3.6077	400.8	1.8076	200.3	"	.4410	.42
36	3.5985	399.8	1.8031	200.2	"	.4340	.16
37	5.6029	622.5	1.8030	200.2	"	.4339	.16

TABLE 1V.

Determination of the Best percent
of Benzene to Use.

Test No.	Bromine Used Wt.	Bromine Used %	Bromine Absorbed Wt.	Bromine Absorbed %	Benzene Used	Benzene Determined	Error %
38	1.8619	207.0	1.6700	185.6	.4392	.4074	-7.22
39	2.4048	251.3	1.7973	199.7	.4392	.4385	.16
40	2.6625	295.7	1.8063	200.4	.4392	.4408	.38
41	3.6025	400.9	1.6072	200.8	.4392	.4409	.39
42	4.5329	503.6	1.7955	199.5	.4392	.4381	-.55
43	5.3345	592.7	1.6009	200.1	.4394	.4394	.00

TABLE V.

Determination of Unsaturated Bodies
in Gasoline.

Test Gasoline No.	Used	Bromine Used	Bromine Absorbed	Bromine = Unsaturated Bodies per cc. of gas
44	1.5cc.	.6625	.0285	0.0190
45	1.5	.6757	.0400	0.0266
46	2.0	.3975	.0180	0.0090
47	"	.3312	.0380	0.0190
49	"	"	.0380	0.0190
50	"	"	.0382	0.0191
51	"	"	.0380	0.0190
52	"	"	.0377	0.0188

TABLE VI.

Determination of Benzene in Gasoline.

Test Gasoline No.	Used	Bromine Used Absorbed	Benzene Determined Gms. per cc.
54	1cc.	1.2179	.3278
56	"	"	.3071
57	"	"	.3140
58	"	"	.3106
61	"	"	.3158
62	"	"	.3140
63	"	"	.3138
64	"	"	.3106
65	"	"	.3158
66	"	"	.3106

TABLE VII.

Test Analyses of Known Mixtures.

Test No.	Bromine Used	Bromine Absorbed	Gas. Used	Benzene Used	Benzene Determined	Error %	
66	1.2179	.6677	1cc.	.1cc	.1654	.1630	-1.46
67	"	.6683	"	"	"	.1668	.80
68	"	.6686	"	"	"	.1673	1.10
69	"	.6679	"	"	"	.1660	.31
70	"	.6675	"	"	"	.1648	-.40
71	"	.6684	"	"	"	.1668	.80
73	1.9154	1.3934	1cc.	.3cc	.3411	.3410	.00
74	"	1.3852	"	"	"	.3380	-.90
75	"	1.4100	"	"	"	.3420	.2
77	"	1.3970	"	"	"	.3410	.00
78	"	1.3790	"	"	"	.3376	-1.00
79	"	1.3701	"	"	"	.3345	-2.00
80	"	1.3725	"	"	"	.3354	-1.71
81	2.6100	2.1130	1cc.	.5cc	.5168	.5150	.36
82	"	2.1100	"	"	"	.5140	.55
84	"	2.1110	"	"	"	.5145	.45
85	"	2.1134	"	"	"	.5152	.30
86	"	2.1900	"	"	"	.5161	.14
87	"	2.0080	"	"	"	.5138	.59
88	"	2.2000	"	"	"	.5164	.09
89	"	2.2090	"	"	"	.5170	.01
91	3.4750	2.4780	1cc.	.6cc	.6046	.6040	.00
92	"	2.5000	"	"	"	.6100	.89
93	"	2.4900	"	"	"	.6070	.39
94	"	2.4800	"	"	"	.6050	.06
96	"	2.5410	"	"	"	.6200	.25
97	"	2.5220	"	"	"	.6150	.17
98	"	2.4980	"	"	"	.6090	.89

TABLE VIll.

Results Using FeCl_3 as a Carrier.

Test No.	Bromine Used Wt.	Bromine Used %	Bromine Absorbed Wt.	Bromine Absorbed %	Benzene Used	Benzene Determined	Error %
99	2.4840	253.8	.3706	41.1	.4392	.0904	79.42
100	"	"	.3105	34.5	"	.0757	82.75
101	"	"	.2588	28.7	"	.0631	85.63
102	"	"	.2174	24.1	"	.0530	87.70
103	"	"	.3500	38.8	"	.0715	83.72
104	"	"	.1373	15.2	"	.0335	92.38
105	"	"	.3968	44.1	"	.0968	77.96
106	"	"	.3086	34.2	"	.0729	82.86
107	"	"	.2734	30.3	"	.0667	84.82
108	"	"	.2543	27.2	"	.0620	85.88

TABLE 1X.

Effects of Presence of Water.

Test No.	Bromine Used		Bromine Absorbed		Benzene		Error
	Wt.	%	Wt.	%	Used	Determined	%
109	2.2289	247.6	.6074	67.5	.4392	.1482	66.26
111	"	"	.4936	54.8	"	.1204	72.58
112	"	"	.5281	58.6	"	.1288	70.39
113	"	"	.2566	28.9	"	.0626	85.75
115	"	"	.3457	38.3	"	.0843	80.57
116	"	"	.5423	60.2	"	.1325	69.33

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